Agarophytes and Carrageenophytes

History of Use and Harvest

Agar is a Malay word for the gel, (which is now known to be a carrageenan) that is part of the cell wall of seaweeds in red algal genus Eucheuma. Its discovery is preserved in a folk legend that originated about 1660. A Japanese emperor and his Royal Party were lost in the mountains during a snowstorm and arriving at a small inn they were ceremoniously treated by the innkeeper, who offered them a seaweed-jelly dish with their dinner. Perhaps the innkeeper prepared too much jelly or the taste was not attractive; in any case, some jelly was thrown away. It froze during the night and, after thawing and draining, was reduced to a thin, papery substance. The innkeeper took the residue and, to his surprise, found that by boiling it up with more water, the jelly could be reconstituted.

In 1881, the German microbiologist Dr. Robert Koch, first established the use of agar in preparing solid culture media for bacteriological research. By 1903, there were 500 factories manufacturing agar in Japan. The California agar industry was developed initially by Dr. Matsuoka in 1921 with U.S. patents for extraction and processing. Horace Selby (the founder of American Agar and Chemical) and C.K. Tseng refined methods prior to and during World War II, when agar was not available from Japan.

Carrageenan, another gel, was originally derived from the red alga, *Chondrus crispus* (Irish Moss), and has a 600 year folk history in Ireland that includes milk puddings thickened by boiling sweetened milk with dried *Chondrus*. The word carrageenan is derived from the colloquial Irish name for this seaweed, carrageen, or *carraigín*; "little rock" (from the Irish place name, probably Carrigeen Head in County Donegal). Since the 1940s, the best-known use of carrageenan has been in products such as chocolate milk and ice cream, but they are also important in other industrial applications.

About 10,000 tons of agar, valued at $200 million, are produced worldwide from species in the red algal families Gelidiaceae and Gracilariaceae. There is currently a shortage of exploitable populations of agar-producing seaweeds; consequently, agar is an expensive product. The best quality agar is extracted from species in the genera *Pterocladia* and *Gelidium*, which are harvested by hand from natural stands in Spain, Portugal, Morocco, the Azores, Mexico, New Zealand, South Africa, India, Chile, Korea and Japan. For *Pterocladia* species, agar quality is low in the colder months and high in the summer. Agars of lesser quality are extracted from *Gracilaria* and *Hypnea* species.

The lower quality, and less expensive, types of agar are used for their gelling and water barrier properties in food products (frozen foods, bakery icings, meringues, dessert gels, candies and fruit juices). As a gelling agent in foods, agar is used at greater than one per cent concentration. For viscosity control and stabilization, lower levels (0.2-0.8 percent) are used. Agar is not assimilated by the human digestive system and, in fact, serves as a laxative. Industrial applications are paper sizing/coating, adhesives, textile printing/dyeing, castings, impressions, etc. The mid-quality agars are used as the gel substrate in biological culture media. Most agar media are made at a 1.0-1.5 percent concentration in water, melt above 185°F and gel at 105°F. They are also important in medical/pharmaceutical fields as bulking agents, laxatives, suppositories, capsules, tablets and anticoagulants. The most highly purified and upper market types (the neutral fractions called agarose) are used in molecular biology for separation sciences (electrophoresis, immunodiffusion and gel chromatography).

Carrageenans are extracted from members of the red algal families Hypneaceae, Phyllophoraceae, Solieriaceae, and Gigartinaceae. *Chondrus crispus* used to be the sole source of carrageenan, but species of *Gymnogongrus, Eucheuma, Ahnfeltia* and *Iridaea* are now used. The market for carrageenan has grown by at least five percent per year for the last 25 years. About 25,000 tons of carrageenan, valued at $200 million, are produced worldwide. *Eucheuma* and *Kappaphycus* are important carrageenan weeds in Hawaii, the Philippines, Indonesia, Malaysia, China and Thailand. In 1996, the Philippines exported $94 million worth of carrageenan from farm raised and natural stands of *Eucheuma cottonii* and *Eucheuma spinosum.* Another principal source is natural populations of *Chondrus crispus* in the Maritime Provinces of Canada, where about 50,000 wet tons are harvested each year.

Carrageenans are far more widely used than agar as emulsifiers/stabilizers in numerous foods, especially milk-based products. It is estimated that the average human consumption of carrageenans in the United States is 250 milligrams (0.01 ounce) a day. Kappa, iota and lambda carrageenans differ in gelling and milk reactivity and are the three most widely used types in commercial products. Kappa carrageenan (extracted chiefly from *Chondrus crispus* and *Eucheuma cottonii*) forms a firm, brittle gel and iota (extracted chiefly from *Eucheuma spinosum*) yields a flexible and dry gel. Lambda carrageenan (extracted chiefly from *Chondrus crispus* and *Gigartina* species) does not gel. Blending of these in different ratios produces different products. Kappa and iota carrageenans are especially important for use in milk products such as chocolate milk, ice cream, evaporated milk, infant formulas, puddings, whipped cream toppings and eggnog, because of their thickening and suspension properties. For these uses, concentrations range from about 0.01 to 0.2 percent. For water-based food products (jellies, jams, salad dressings, syrups, dessert gels, meat products and pet foods), carrageenan concentrations are somewhat higher (0.2-0.5 percent). Industrial products incorporating carrageenans are air freshener gels, cleaners, etc. Pharmaceutical and medical applications are similar to those of agar.

Status of Biological Knowledge

Agar and carrageenan are phycocolloids derived from galactan polysaccharides, the major polysaccharide constituents of the cell walls of most marine red algae. The types and quantity vary from species to species; this is an important character in biosystematics. The amount present also varies with ecological factors such as light, nutrients, wave exposure, and temperature. Polysaccharides have an important role in the biology of these algae, including protection from wave action, physical support of cells, ion exchange, water binding for protection from desiccation. The galactans have a common backbone which consists of galactose units linked alternately by ð(1-3) and ß(1-4). The alpha (ð) unit is linked to either D- or L-galactose whereas the beta (ß) unit is always linked to D-galactose. In agar the ð-linkages are all with L-galactose and in carrageenan they are all with D-galactose. (For pictures of these structures, see www.rrz.uni-hamburg.de/biologie/b_online/e26/26d.htm) The chemistry of these polymers is complex.

Status of the Beds

There are many genera of red algae in California that yield agars and carrageenans. The most common and abundant agar weeds in California are species in the genera *Gelidium* and *Pterocladia* (family Gelidiaceae) and *Gracilaria* and *Gracilariopsis* (family Gracilariaceae). Of the six species of *Gelidium* in California, only *G. robustum* is available in sufficient wild stocks to warrant limited harvest for agar production. Before and during World War II and until American Agar and Chemical Company in San Diego closed in about 1986, *G. robustum* was collected by divers along the southern California coast. Resource management of wild stock of *G. robustum* was investigated carefully to establish control of season, amount and method of harvesting, but it proved difficult to enforce regulations. Today, there is no harvest of wild stocks for commercial agar production in California, but wild stocks are still harvested in Baja California, Mexico, by local fisherman for processing in Ensenada and a subsequent export of refined agar. *Gelidium robustum* is very slow growing in nature and even slower in mariculture, thus making it unlikely as a major resource. Several other species, including *G. coulteri,* show much faster growth in nature and in tank culture, providing an acceptable quality agar. Unfortunately, the cost of these culture systems in California is too high for competition with either wild stock harvest or cultivation in other countries. *Gracilaria* and *Gracilariopsis* species in California and elsewhere offer considerable potential, because of their fast growth and yield of agar. Several species are extensively cultivated in Chile, China and Thailand, for example, contributing 50 percent of worldwide agar production; several countries (e.g., South Africa and New Zealand) are studying the possibility of mariculture. The best candidate for large-scale culture in California is *Gracilariopsis lemaneformis.* Although extensively cultivated in open bays of other countries, it is unlikely that such cultivation could occur in California, because of government restrictions.

The carrageenan weeds common in California are members of the genera *Mazzaella, Mastocarpus, Rhodoglossum* and *Sarcodiotheca.* Several California species can be grown successfully in mariculture, but the low value of carrageenan makes both wild harvest and culture economically unrealistic. Compared to agars, carrageenans generally are more plentiful and less costly, because the carrageenan weeds are widely available from harvest of wild stocks and extensive cultivated stocks in Canada and the tropics. Genetic manipulation and cell culture of *Chondrus crispus* are being explored to produce novel carrageenans to stimulate the possibility of mariculture on the East Coast of the United States.

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